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ORIGINAL PAPER

Assessment of heavy metals in sediment and in suspended particles affected by multiple anthropogenic contributions in harbours

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Abstract La Goulette, Rades and Sidi Bou Said harbours are considered as the most important commercial and tourist ports in the Gulf of Tunis. They are located on the northeast coast of Tunis and receive industrial and municipal wastewaters from Tunis city. The contamination level of copper, lead, zinc, cadmium, manganese, iron, total nitrogen and total organic carbon in the surface sediments was assessed on the basis of the enrichment index factors and corresponding to sediment quality guidelines. The results revealed moderate to highly elevated concentrations near to the sites of intense industrial, shipping and/or commercial activities suggesting a direct influence of these sources. In winter and summer, concentrations varied for cadmium, 0.28–1.40 mg kg^{-1}; lead, 18–217 mg kg^{-1}; zinc, 87–459 mg kg^{-1}; copper, 8–121 mg kg^{-1}; manganese, 208–254 mg kg^{-1}; and for iron, 24–40 g kg^{-1}. Furthermore, in summer the concentration of the total organic carbon and the total nitrogen contents range between 4.3–6.5 % and 0.06–0.49 % with an average value of 5.9 and 0.15 %, respectively. Whereas, in winter, total organic carbon and the total nitrogen concentrations varied between 2.3–9.6 % and 0.03–0.22 % with an average value of 6.1 and 0.14 %, respectively. The levels of lead, copper, zinc and iron in suspended particulate matter content range between 3.1–27.5 mg kg^{-1}; 0.4–11.7 mg kg^{-1}; 1–1.5 mg kg^{-1}; 1.2–1.7 g kg^{-1}, respectively. This study revealed that heavy metals pollution is mainly localized in the commercial (Rades) and fishing (La Goulette) harbours and not in the yachting (Sidi Bou Said) harbour.

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Introduction

Harbours are generally enclosed areas, characterized by high levels of pollution in water and sediment, a low oxygen concentration in the water column, and a low biodiversity of benthic communities such as Crustacean, Molluscs, Annelids (Choueri et al. 2010; Hayward et al. 1997; Labonne et al. 2001). In the design and planning of a harbour, civil engineers and policy-makers are concerned with the quality of the contained water, which is dependent upon the basin's flushing rate and the human activities within or adjacent to the harbour (Breslin and Sanudo-wilhelmi 1999; Muniz et al. 2004; Romano et al. 2004; Yin et al. 2000). In addition, the water metallic contaminants associated with sediments showed various behaviours depending on physicochemical conditions.

Heavy metal distributions in surface sediment provide a long-term, integrated assessment of contaminant supply in depositional estuarine environments, whereas suspended particulate matter (SPM) chemistry gives information on short-term processes controlling supply and dispersion (Birch and O'Hea 2007; Serpaud et al. 2004). The partitioning of trace metals within SPM is an important factor influencing trace metal adsorption, bioavailability, transport and fate in natural waters (Lu and Allen 2001; Saeedi et al. 2004).

La Goulette (G: passenger and P: fishing traffic), Rades (RD: commerce) and Sidi Bou Said (SB: yachting) are considered as the principal harbours in the west coastal of the Gulf of Tunis. Harbours received municipal wastewaters (either untreated or with only primary treatment) from the neighbouring cities. In addition, harbours of La Goulette and Rades are the receptor of multiple industrial activities (e.g., chemical manufacturing plants, metal processing factories, and electronic and mechanic industries), commercial discharges and passenger traffic. As mentioned by Mzoughi and Chouba (2011), contamination appears to be related to local input and seems to suggest localized sources influenced by industrial use, air deposition and uncontrolled discharge which could serve as important pathways for organic and inorganic compound inputs to all harbours.

Therefore, the present harbours represent a useful case study at the investigating level, assessment and distribution of heavy metal contamination in sediment and in suspended particulate matter of the Mediterranean harbour area. To our knowledge, no previous study was conducted on these harbours and this investigation provides a pioneer picture of metal contaminations of these areas, thus providing a better understanding of the contamination sources in these industrialized, fishing and commercial areas of the Mediterranean basin.

Sediment is a composite material consisted of inorganic components, mineral particulates and organic matter at various stages of decomposition. It is considered a suitable medium to study the contamination of aquatic environments as it represents the sink of multiple contaminant sources (Lager et al. 2005; Zhou and Rowland 1997). Moreover, dredging is necessary to maintain or improve extend navigable depths in harbours which are usually a statutory requirement for port and harbour authorities.

This sediment quality can strongly influence distributions of benthic animals and plants which in return can influence fisheries and bird life (Choueri et al. 2009; Mzoughi and Chouba 2005; Zvinowanda et al. 2009). Polluted sediment can feed back negatively by releasing contaminants that act directly on organisms and microorganisms or indirectly through water de-oxygenation.

The aim of the present research is to assess and examine the distribution and sources of heavy metal pollution in sediment and in SPM collected during summer 2008 and winter 2009 from La Goulette, Rades and Sidi Bou Said harbours in the Gulf of Tunis.

Materials and methods

Study area

Harbours of Rades (RD); La Goulette (passenger G); La Goulette (fishing P) and Sidi Bou Said (SB) are situated in the northwest part of Tunis Gulf (36°48N–36°52N and 10°18E–10°21E) (Fig. 1). Among them, Rades and La Goulette harbours are the most important in Tunisia, because of their special geographical locations and their communication with the channel of Tunis. In fact, the channel communicates with the sea and increases water exchange. These harbours are constantly threatened by contamination due to their proximity to human settlements (sewage) and high economic and industrial activities adjacent in these harbours sites. Sidi Bou Said harbour has an important pleasure boating activity.

The sampling was realized in summer 2008 and in winter 2009 using a global positioning system (GPS) (Table 1). Three sampling stations were chosen to provide good area coverage in each harbour studied (Fig. 1). The depth of the different sampling stations varied from 3 to 17 m (Table 1). Surface sediments were collected using a Van Veen grab (surface area is 0.1 m^2). Sediment samples were stored immediately in a freezer (−20 °C) until analysis.

Sediment samples were freeze-dried, and sieved through vibrating stainless sieves with mesh sizes of 2 mm to 63 µm. The fine fraction (<63 µm) was collected and analyzed. This fraction of sediments contains higher concentrations of mineral elements than the sand fraction (Tam and Wong 2000) and metals are most often associated with small grains (Morillo et al. 2004). Traditionally, the fine-grained fraction of the sediment has been used to examine metal contamination in sediments. The clay fraction is known to be the most important substrate for metal attachment, and metal concentrations tend to increase from sand to silt (Tam and Wong 2000).

Surface water samples (20 L), were collected in pre-cleaned 20 L amber glass bottles and vacuum filtered through 0.45 µm glass fibre filters to obtain SPM. The membrane filters of SPM were freeze-dried and stored until metal analysis (Etcheber and Jouanneau 1980).

Total organic carbon (TOC) and total nitrogen (TN) were determined using CHNS/O elemental analyzer 2400 series II (Froelich 1980; Hedges and Stern 1984) in sediment. The subsamples for TOC were obtained by adding 1 M hydrochloric acid (HCl) and dried at 60 °C. Replicate analysis gave a CV 0.9 % for TOC and 1.3 % for TN.

Analytical procedures

Digestion of Cd, Pb Cu, Zn, Fe and Mn was carried out in a Teflon bombs with 5 mL nitric acids (HNO_3) and 6 mL fluorhydric acids (HF), using a microwave (Millestone type Ethos) digestion at 100 % power with pressure set at 120 psi for 25 min, the overall digestion time for the cycle was 40 min. Blank acid mixtures were digested in the same way. Boric acid (H_3BO_3) (0.8 g) was added and the samples were then diluted to 50 mL with milliQ water.

Analysis were performed by atomic absorption spectrometry (AAS, type Varian 220Z) equipped with Zeeman correction. Analysis of Zn ($\lambda = 213.9$ nm), Mn

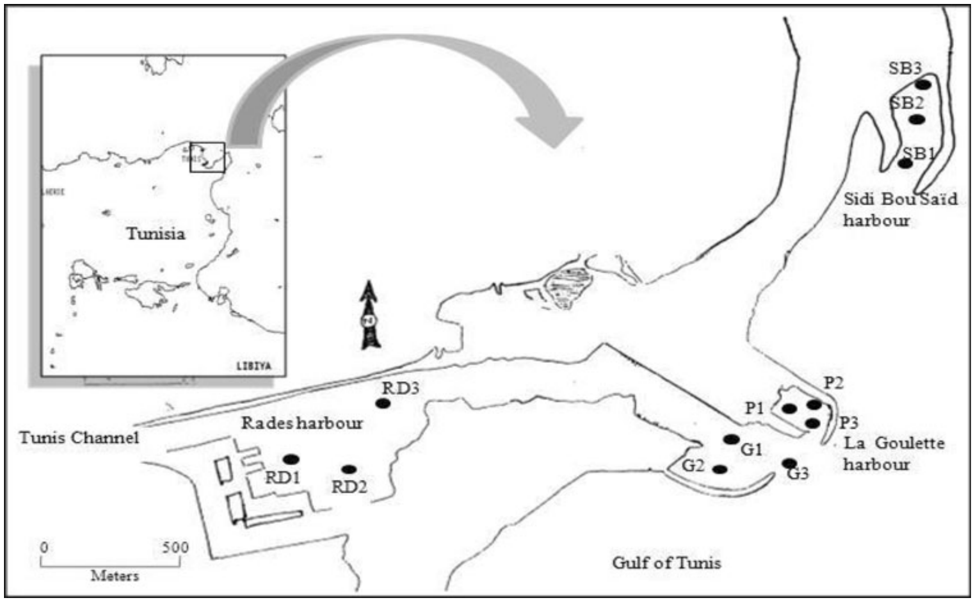

Fig. 1 Location map of studied samples

Table 1 Description of samples collected from Rades (Rd), La Goulette (G), Fishing (P), and Sidi Bou Saïd (SB) harbours

Stations	Latitude	Longitude	Water depth (m)	Temprature (°C)	Salinity (PSU)	Summer Total N (%)	Winter Total N (%)	Summer TOC (%)	Winter TOC (%)
RD1	36°4,823	10°2,300	17	14.6	35.4	0.49	0.20	6.4	4.9
RD2	36°4,830	10°1,623	12	14.9	35.3	0.10	0.20	6.5	6.9
RD3	36°4,837	10°1,701	3	14.2	35.5	0.14	0.21	6.1	7.8
G1	36°4,833	10°1,752	12	14.3	35.8	0.06	0.16	6.1	6.9
G2	36°4,827	10°1,807	12	14.2	35.5	0.07	0.14	5.8	5.1
G3	36°4,815	10°1,835	12	14.1	35.9	0.07	0.08	6.1	5.6
P1	36°4,830	10°1,827	4.5	13.8	35.9	0.09	0.22	6.5	9.6
P2	36°4,830	10°1,833	4.5	14.6	35.7	0.05	0.17	6.3	4.6
P3	36°4,823	10°1,835	3	15.1	35.5	0.07	0.03	5.7	7.7
SB1	36°5,157	10°2,103	3.5	14.1	36	0.23	0.10	5.9	4.8
SB2	36°5,158	10°2,103	3.5	14.8	36.7	0.29	0.09	5.7	7.1
SB3	36°5,153	10°2,101	3	15	36	0.10	0.03	4.3	2.3

($\lambda = 279.5$ nm) and Fe ($\lambda = 248.3$ nm) were performed by flame AAS, whereas Cu ($\lambda = 327.4$ nm), Pb ($\lambda = 283.3$ nm) and Cd ($\lambda = 228.8$ nm) were analyzed by electrothermal AAS equipped with graphite furnace. The instrument was calibrated using standard stocks for each element. The accuracy and precision of the overall procedure have been determined and are estimated to 5 % for most elements. The quality assurance of the analytical results was controlled with the use of certified reference materials (CRM, marine sediment, IAEA-405) provided by International Atomic Energy Agency, Monaco).

Replicated ($n = 3$) measures of CMR and reagent blanks, were used to assess accuracy (estimated as >95 %). The analytical precision was generally better than 6 %.

Statistical analyses

The multivariate analytical tool (ANOVA) was used to assess the difference of heavy metal mean concentrations found between seasons (summer and winter) and between harbours [La Goulette (G and P), Rades (RD) and Sidi Bou Saïd (SB)]. The difference is considered statistically significant when $P < 0.05$. To interpret statistically significant, a Tukey post hoc test was carried out and the principal component analysis (PCA) was employed for 12 samples, 6 heavy metals and for the TOC distribution. Correlation test was applied for the heavy metal concentrations in summer and winter. All statistical analyses were performed using Statistica 6 software package.

Results and discussion

Sediment characteristics

Harbour sediments showed a different nature composition. The top layer of samples was brownish or grey in colour. The sample of the fishing (P) harbour contained less sand fraction than the harbours of La Goulette and Rades (G, RD). The percentage of fine fraction particle (<63 μm) varied between 2 and 25 %.

The distribution of total organic carbon (TOC) in different harbours study contents range between 4.3 and 6.5 %, with an average value of 5.9 % in summer and between 2.3 and 9.6 %, with an average value of 6.1 % in winter. No correlation was obtained for TOC with the distribution of either metals in sediment or in SPM, suggesting a dominant role of anthropic sources of metals. The percentage of total nitrogen in different harbours varied between 0.03 and 0.49 %. The maximum was found in Rades harbour and minimum in Sidi Bou Said (Table 1). Similar percentile values were obtained in Ceuta harbour (Guerra-Garcia and Garcia-Gomez 2005).

Heavy metals distribution and sources

Metal concentrations in summer and winter found in sediment harbours varied between (1.586–0.242 μg g^{-} dw (dry weight) for Cd, (527–70 μg g^{-1} dw) for Zn, (246–12 μg g^{-1} dw) for Pb, (132–7 μg g^{-1} dw) for Cu, (45–25 mg g^{-1} dw) for Fe and (281–173 μg g^{-1} dw for Mn (Fig. 2).

Concentration difference test was carried out for the heavy metals in sediment between the four sampling areas. Significant result differences ($P < 0.05$) showed the same evolution profile for the following metals: Cd, Pb, Zn and Cu. On the other hand, no significant difference was noticed for the Mn and Fe metals.

Generally, the highest concentration of all metals analyzed in summer and in winter was registered in sediment for all stations from Rades (RD) (industrial area) and La Goulette (P) (fishing) harbours (Fig. 2) indicating the presence of local source of contamination. It could be attributed to several reasons as these harbours are characterized by the discharge materials, activities of fishing, antifouling paint and the two steam electric power plants located near the harbour and drainage sewage in this zone. The lowest metal contents were measured in Sidi Bou Said harbour (yachting) in summer and in winter sediment, only copper showed an important level after fishing harbour (P). This is especially due to antifouling paints used for ships and yacht club in the harbour.

The salinity and nitrogen found in Rades harbour confirm these sources (Table 1). It seems that the hydraulic regime within the harbour as well as the turbulence of the sea bed caused by the ship engines are significant agents in the deposition of the contaminants in Rades and La Goulette harbours. Moreover, it has been demonstrated by Chen et al. (2007) and Mohiuddin et al. (2010) that metal concentrations correlated closely to the physical–chemical properties of the sediments, which strongly suggested the influence of industrial and municipal wastewaters discharged.

Pb, Cu, Zn and Fe were found in SPM. Whereas Cd and Mn were not detected (Table 2). Correlation (r^2) obtained for TOC and for Pb, Cu, Zn and Fe were 0.03, 0.03, 0.16 and 0.07, respectively. This indicates that TOC is not responsible for dictating the distribution of metals in SPM.

Yacht (pleasure) boating activity and the maintenance of boats are shed from abandoned structures represent a highly significant, heterogeneous source of metallic particle contamination in the Sidi Bou Said (SB) harbour. These activities explained the source of Cu and Zn in SPM. Copper- and Zinc-based antifouling paints and cathodic protection devices have been previously identified as important sources of these metals in estuaries and harbour sediments (Uncles et al. 2000; Trefry et al. 1994; Turner 2010; Zwolsman and Gijsbertus 1999). These values observed in the SPM are due probably to the fine particles generated by sanding or blasting of boat hulls or that are produced gradually by antifouling paint (Turner 2010).

The concentrations of Pb, Cu, Zn, and Fe in SPM of different harbours are much lower than those found in other harbours (Palanques 1994).

Birch and O'Hea (2007) explained that the high concentration of Cu and Zn in SPM caused by the difference of metal dissolutions. However, dissolved Cu concentrations increased with the increasing ambient energy, i.e. from quiescent to high precipitation to high rainfall/high wind conditions, and dissolved Zn concentrations the highest during high precipitation. SPM are transported primarily as flocs comprising a composite structure of organic/inorganic particles and microbial communities. During transport particles are in a constant state of physical and chemical change. Flocculation and de-flocculation alter the surface area of the particle available for adsorption, which may affect partitioning of trace contaminants between solid and dissolved phases.

The concentration of Fe, Pb and Cu metals in the sediments and in SPM was not correlated. However, high correlation was demonstrated in other study (Hatji et al. 2003; Palanques 1994) indicating that the dispersion of metals in SPM is mainly controlled by the harbour and severely affected by untreated or partially treated industrial effluents and municipal sewages.

Partitioning of metals between SPM and sediment is not only related to their solubility and availability, but also

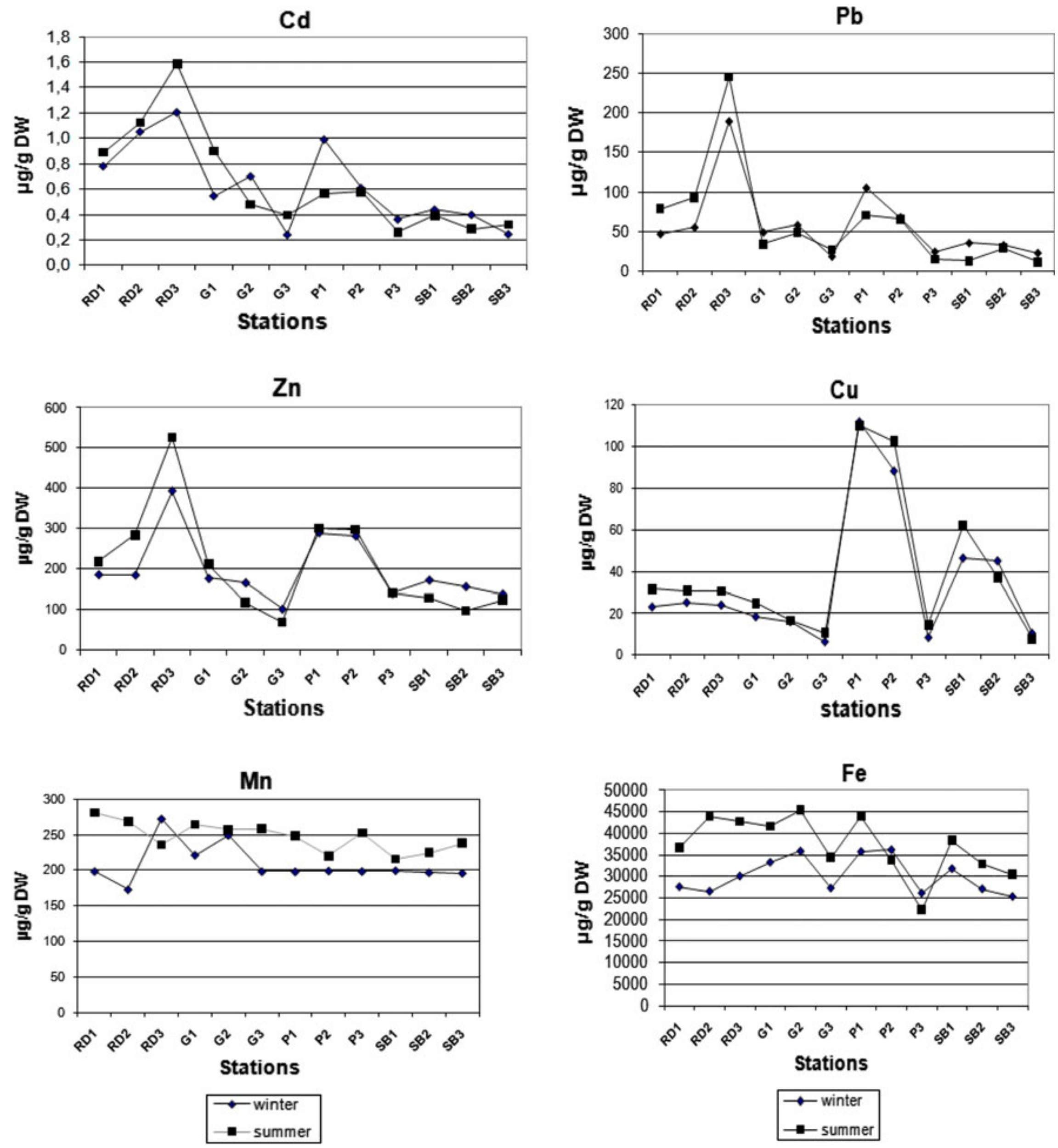

Fig. 2 Concentrations (µg g^{-1} dw) of Cd, Pb, Zn, Cu, Mn and Fe in sediment collected from Rades, La Goulette (fishing and passenger), and Sidi Bou Said (yachting) harbours

depends on structural and physicochemical properties, diagenetic mobilization of trace metals, vicinity and nature of the particles (Palanques 1994).

The heavy metal contents in sediments and SPM varied between stations, it could be due to the re-suspension phenomenon induced by wave and tide currents, benthic organisms and anthropogenic activities. Metal-rich particles introduced into the water column during re-suspension may also release adsorbed phases due to changes in environmental conditions, including pH and redox conditions, light availability, wind, temperature and salinity (Filgueiras et al. 2004). These processes may contribute to the delivery of metals from the bottom sediment (Turner et al. 2004).

Index of contamination

The assessment of the pollution degree, through the determination of the metal levels in surface sediments, is an approach which is not very significant. Thus Ben Bouih et al. (2005) and Boust et al. (1980) express the metallic contamination using the contamination factor Fm (measured content/reference content), Fm >1 and the index contamination Im.

Table 2 Concentrations of Pb, Cu, Fe, Zn, Cd and Mn in the SPM (μg g^{-1}) La Goulette (fishing and passenger), Rades (commercial) and Sidi Bou Saïd (yachting) harbours

Stations	Pb	Cu	Fe (10^3)	Zn (10^2)	Cd	Mn
RD1	6.23	2.33	1.22	1.28	ND	ND
RD2	7.93	2.53	1.24	1.27	ND	ND
RD3	14.91	3.47	1.44	1.30	ND	ND
G1	27.49	4.90	1.58	1.45	ND	ND
G2	4.42	1.17	1.54	1.18	ND	ND
G3	3.09	1.15	1.43	1.13	ND	ND
P1	4.41	0.43	1.39	1.01	ND	ND
P2	27.12	0.55	1.73	1.49	ND	ND
P3	9.75	0.48	1.34	1.17	ND	ND
SB1	8.30	11.40	1.43	1.23	ND	ND
SB2	7.69	11.72	1.31	1.19	ND	ND
SB3	5.25	8.53	1.43	1.48	ND	ND

ND not detectable

$\mathrm{Im} = 1/n \sum \mathrm{Fm}$, with n the number of element scanned when Im is superior to 2, consequently, contamination with heavy metals is considered significant.

When applying the factor metal index, Fm values can be classed as Zn > Fe > Cu > Pb > Cd > Mn. The average indexes of the studied harbour contamination were between 0.8 and 8. These values explained the high contamination of sediments with Cd, Zn and Pb, particularly in Rades and La Goulette (fishing) harbours. It could be attributed to the deposition of the dissolved and particulate heavy metals and their compounds in the water column through sewage outfalls. In addition, heavy metals can be introduced by ships (cargo, fuel, paints, etc.) and industrial activities in the wider area.

The index Im in La Goulette (G) and Sidi Bous Said (SB) harbour stations was 1.12 and 1.40, respectively; indicating a moderate contamination level with Cu and Cd compared to the other harbours. Based on results published by Ligero et al. (2002) and Long et al. (1995), we can conclude that all the harbour sediments have toxic concentrations of Cd, Zn, Pb, Cu since they exceed both ERL (1.2, 150, 46.7, 34 mg kg^{-1}, respectively) and ERM (9.6, 410, 218, 270 mg kg^{-1}, respectively) guidelines. In the present study, the comparison of Cd, Zn, Pb and Cu concentrations in Rades sediment harbour stations (commercial) with the corresponding ERL/ERM established values, leads us to consider it as polluted marine sediment. In La Goulette (fishing) harbour sediment, Pb, Zn and Cu concentrations were superior to the toxic effect range ERL and lower than ERM. Hence, it is considered as heavily contaminated up to polluted with Zn, Pb and Cu. On the other hand, concentration of Zn and Pb in La Goulette (passenger) harbour is higher than ERL and lower than ERM, and corresponds to medium polluted marine sediments. The same results were obtained for Sidi Bou Saïd harbour, regarding Cu and Zn concentrations.

Table 3 Pearson correlation coefficient matrix between the trace elements and TOC in summer

Variable (summer)	Zn	Fe	Mn	Cd	Pb	Cu	TOC
Zn	1.00						
Fe	0.43	1.00					
Mn	−0.02	0.21	1.00				
Cd	0.86	0.59	0.26	1.00			
Pb	0.92	0.46	0.04	0.89	1.00		
Cu	0.33	0.24	−0.42	0.01	0.09	1.00	
TOC	0.42	0.49	0.30	0.50	0.37	0.47	1.00

Table 4 Pearson correlation coefficient matrix between the trace elements and TOC in winter

Variable (winter)	Zn	Fe	Mn	Cd	Pb	Cu	TOC
Zn	1.00						
Fe	0.51	1.00					
Mn	0.44	0.37	1.00				
Cd	0.78	0.30	0.36	1.00			
Pb	0.92	0.36	0.68	0.82	1.00		
Cu	0.65	0.62	−0.19	0.31	0.32	1.00	
TOC	0.50	0.18	0.13	0.46	0.48	0.39	1.00

Put together, the heavy metal contaminations obtained for surface sediments in the different studied harbours can be attributed to the metal nature, intensive maritime activities in summer and to different sources of metals in each harbour. High values observed in Rades and La Goulette (fishing) stations are probably due to the sewage outfall, as well as to steam electric power plants located near harbours, and to pollutants from the ships and the industries (Mzoughi and Chouba 2011).

Tables 3 and 4 present the Pearson correlation coefficient matrix between the various heavy metals and TOC. Cd, Pb and Cu were significantly correlated with Zn, indicating common origin, probably due to the sewage outfall in regions bordering harbours. Zn showed to be the most labile metal recovered in the first extraction stages, and was associated with the non-residual fraction of sediment (Caplat et al. 2005).

Furthermore, the good correlation between Pb with Cd and Mn could reflect adsorption of Pb and Cd by Mn oxides. Similarly, the positive correlation of Cu with Fe probably indicates that a part of the Cu content was adsorbed by sediment (Tables 3, 4).

To understand the distribution modes (similarities/dissimilarities) of the different heavy metals, to compare

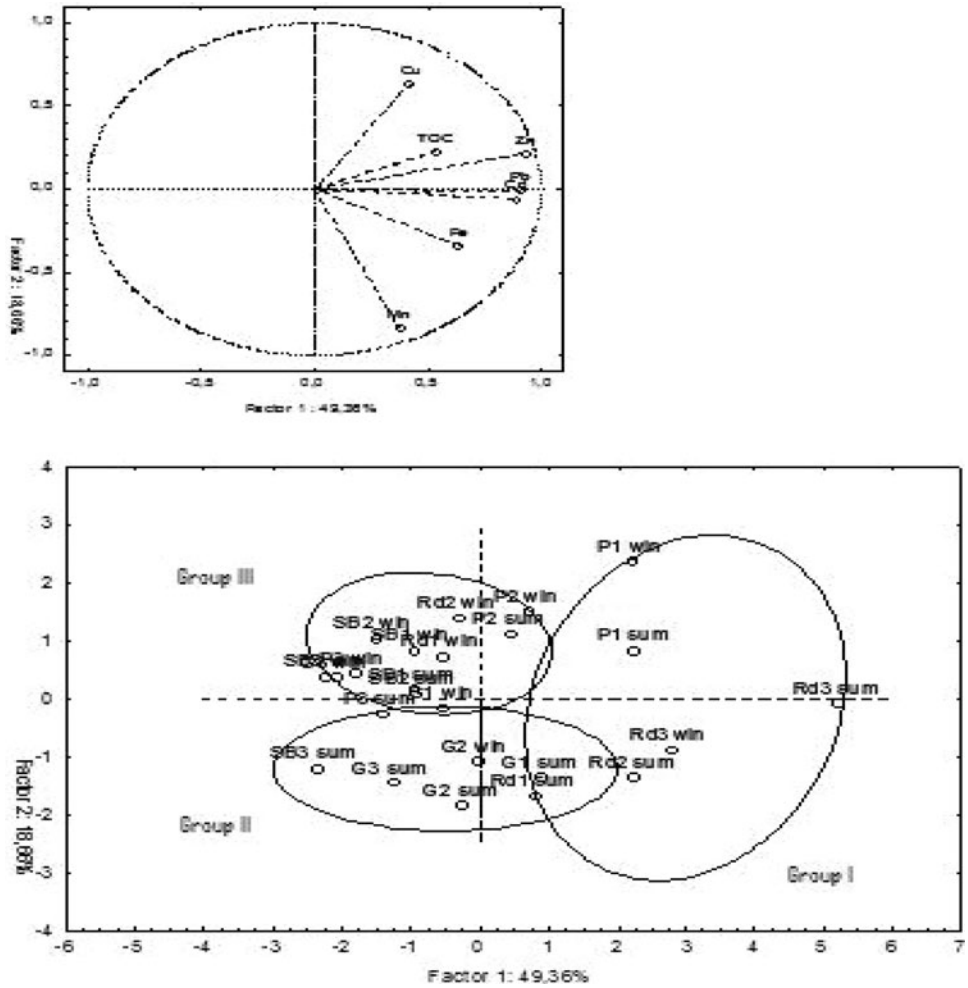

Fig. 3 Principal component analysis for trace metals and total organic carbon in La Goulette, Rades and Sidi Bou Saïd harbours

between sample parameters and original regions, as well as to elucidate possible metal sources, a principal component analysis (PCA) was employed.

The two principal components account for 68.02 % of the total variance (Fig. 3). The first factor (PC1) associated positively with the Cd, Pb and Zn accounted for almost 49.36 % of the variability. The second factor (PC2) associated with Mn, Fe, Cu and TOC, accounted for 18.66 % of the variance.

Analysis result clustered three main groups showing an evident difference of heavy metal distribution patterns (Fig. 3); the shipping, passenger and the commercial areas.

Group I is formed by six stations (Rd1win, Rd1sum, Rd2win, P1win, P2sum and P2win) representing a strong evidence of possible impacts from wastewater discharge in Tunis station. Stations belonging to this group also exhibited hydrocarbon spills and/or shipyard and industrial activities where metals extensively used in alloys and metallurgical materials located at the inner part of the harbour (commercial activity).

The second group II (G2sum, G2win, G3sum, Rd2sum, G1win, P3sum, SB3sum and SB1sum) could be related to anthropogenic activities (passenger activity).

The third group III (SB1win, SB3win, SB2sum, SB2 win, G3win, P3win and P3win) could display pollution by the presence of important shipyard and fishing that also exhibited high Zn and Cu metals (fishing and yachting activity).

The high concentrations of Cd, Pb, Zn and Fe in the commercial area (RD) may be related to the important influence of urban and industrial wastewaters. Moreover, the vehicle emissions associated to the high traffic volume recorded (close to the commercial district of the harbour) may represent a major source of Pb and secondarily of Zn to marine sediments.

On the other hand, elevated concentrations of Cu and Zn in fishing and yachting harbours are due to the washout of the antifouling paints used for ships in the harbour of P and SB. Finally, the position of passenger harbour (G) (communicate with the Gulf of Tunis) showed a negative correlation with the major metals.

Table 5 Concentration of Cd, Zn, Pb, Cu, Mn and Fe (µg g^{-1}) in marine sediments of different Mediterranean harbours

Area		Cd	Zn	Pb	Cu	Mn	Fe	References
Rhodes harbour, Greece		0.003–0.08	59–168	77.7–152	38.3–64.7	162–181	–	Angelidis and Aloupi (1995)
Mandraki harbour, Rhodes, Greece		0.03–0.04	211–242	133–230	72.3–101	138–154	–	Angelidis and Aloupi (1995)
Keratsini harbour, Greece		190–1,763	409–6,725	521–1,263	195–518	95–1,101		Galanopoulou et al. (2009)
Naples harbour, Italy		0.2–2.5	41–1,196	37–314	40–415	95–535		Adamo et al. (2005)
		0.9	303	123	68	389		
Port of Naples (southern Italy)		0.01–3	17–7,234	19–3,083	12–5,743			Sprovieri et al. (2007)
Barcelona harbour		0.4–2.7	1.13–180	85–589	45–110	70–530		Guevara-Riba et al. (2004)
Goulette harbour, Tunisia	(G)	0.32–0.72	87–194	23–54	8–22	228–253	30,792–40,628	Present study
Rades harbour, Tunisia	(Rd)	0.84–1.40	203–459	63–217	27–28	221–254	32,104–36,388	Present study
Sidi Bousaid harbour, Tunisia	(SB)	0.28–0.42	128–151	18–31	9–54	208–217	27,830–35,067	Present study
Goulette Fishing harbour, Tunisia	(P)	0.31–0.78	141–326	20–88	12–121	210–225	24,156–39,860	Present study

A comparison of the above-mentioned concentrations with corresponding values obtained in Naples (Italy) and Rhodes (Greece) harbours (Table 5). An exception has been accorded to Cd, Pb, Zn, and Cu found in the surface sediments of Rades harbour which showed higher concentration than those found in the harbour of Rhodes in Greece.

Conclusion

The analytical determinations of total metal content in four harbours (Rades (commerce), La Goulette (passenger and fishing), and Sidi Bousaid (yachting)) situated in the north of Tunis represent a useful data to define the quality of marine environment in this region. The results of the chemical analysis in sediment and in SPM showed that Cd, Cu, Zn, Pb, Fe and Mn proved to be an important anthropic contribution with a spatial pattern distribution that clearly reflects the different influence of industrial and/or commercial activities located in the various areas of the harbour. Potential risk associated to the relatively high contents of these heavy metals in the surface sediments of the Rades harbour is related to the wastewaters. Tunis station that also exhibited hydrocarbon spills and/or shipyard and industrial activities as well as to steam electric power plants located in the near harbours. Harbours activities and their geographical position have an important influence on metals distribution in SPM and surface sediment in different harbours. Heavy metal concentrations found in the present study were comparable to other Mediterranean harbours and based on the standard quality guidelines used in the present study, it can be suggested that Rades and La Goulette (fishing) harbours as polluted area and Sidi Bou Said as moderately polluted harbour. Within this study, it was demonstrated that Cd, Pb and Zn are responsible for large spatial variations explaining 47 % of the total variance, whilst Mn, Fe, Cu and TOC explain only 20.11 % of the total variance.

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References

Adamo P, Arienzo M, Imperato M, Naimo D, Nardi G, Stanzione D (2005) Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. Chemosphere 61:800–809

Angelidis MO, Aloupi M (1995) Metals in sediments of Rhodes harbour, Greece. Mar Pollut Bull 31:273–276

Ben Bouih HN, Bassali H, Leblans M, Srhiri A (2005) Contamination en métaux traces des sédiments du lac Fouarat (Maroc). Afrique Sci 1:109–125

Birch G, O'Hea EL (2007) The chemistry of suspended particulate material in a highly contaminated embayment of Port Jackson (Australia) under quiescent, high-wind and heavy-rainfall conditions. Environ Geol 53:501–551

Boust D, Jouanneau JM, Latouche C (1980) Méthodologie et interprétation des teneurs totales en métaux traces contenus dans les sédiments estuariens et littoraux. Bull Inst Géol Bassin d'aquitaine 30:71–86

Breslin VT, Sanudo-wilhelmi S (1999) High spatial resolution sampling of metals in the sediment and water column in Port Jefferson Harbor, New York. Estuaries 22(3):669–680

Caplat C, Texier H, Barillier D, Lelievre C (2005) Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin. Mar Pollut Bull 50:504–511

Chen C-W, Kao C-M, Chen C-F, Dong C-D (2007) Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere 66:1431–1440

Choueri RB, Cesar A, Abessa DMS, Torres RJ, Morais RD, Riba I, Pereira CDS, Nascimento MRL, Mozeto AA, DelValls TA (2009) Development of site-specific sediment quality guidelines for North and South Atlantic littoral zones: comparison against national and international sediment quality benchmarks. J Hazard Mat 170:320–331

Choueri RB, Cesar A, Abessa DMS, Torres RJ, Riba I, Pereira CDS, Nascimento MRL, Morais RD, Mozeto AA, DelValls TA (2010) Harmonised framework for ecological risk assessment of sediments from ports and estuarine zones of North and South Atlantic. Ecotoxicology 19(4):678–696

Etcheber H, Jouanneau JM (1980) Comparison of the different methods for the recovery of suspended matter from estuarine waters: deposition, filtration and centrifugation; consequences for the determination of some heavy metals. Estuarine Coast Mar Sci 11:701–707

Filgueiras AV, Lavilla I, Bendicho C (2004) Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: a case study. Sci Total Environ 330:115–129

Froelich S (1980) Studies of the reproduction nutrition and symbiosis with zooxanthellae of the temperate scleractinian coral Astrangia danae. PhD dissertation. University of Rhode Island, p. 191

Galanopoulou S, Vgenopoulos A, Conispoliatis N (2009) Anthropogenic heavy metal pollution in the surficial sediments of the Keratsini Harbor, Saronikos Gulf, Greece. Water Air Soil Pollut 202:121–130

Guerra-Garcia JM, Garcia-Gomez JC (2005) Oxygen levels versus chemical pollutants: do they have similar influence on macrofaunal assemblages: a case study in a harbour with two opposing entrances. Environ Pollut 135:281–291

Guevara-Riba A, Sahuquillo A, Rubio R, Rauret G (2004) Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. Sci Total Environ 321:241–255

Hatji V, Apte SC, Hales LT, Birch GF (2003) Dissolved trace metal distributions in Port Jackson estuary (Sydney Harbour), Australia. Mar Pollut Bull 46:719–730

Hayward BW, Stephenson AB, Morley MS, Riley J, Grenfell HR (1997) Faunal changes in Waitemata Harbor sediments, 1930s–1990s. J Royal Soc New Zealand 27:1–20

Hedges JI, Stern JH (1984) Carbon and nitrogen determinations of carbonate-containing solids. Limnol Oceanogr 29:657–663

Labonne M, Ben Othman D, Luck JM (2001) Pb isotopes in mussels as tracers of metal sources and water movements in a lagoon Thau Basin, S. France. Chem Geol 181:181–191

Lager T, Hamer K, Schulz HD (2005) Mobility of heavy metals in harbor sediments: an environmental aspect for the reuse of contaminated dredged sediments. Environ Geol 48:92–100

Ligero RA, Barbera M, Casas-Ruiz M, Sales D, Lopez-Aguayo F (2002) Dating of marine sediments and time evolution of heavy metal concentration in the Bay of Cadiz, Spain. Environ Pollut 118:97–108

Long ER, MacDonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manage 19:81–97

Lu Y, Allen HE (2001) Partitioning of copper onto suspended particulate matter in river waters. Sci Total Environ 277: 119–132

Mohiuddin KM, Zakir HM, Otomo K, Sharmin S, Shikazono N (2010) Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. Int J Environ Sci Tech 7(1):17–28

Morillo J, Usero J, Gracia I (2004) Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere 55:431–442

Muniz P, Danulat E, Yannicelli B, García-Alonso J, Medina G, Bícego MC (2004) Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo harbour (Uruguay). Environ Int 29:1019–1028

Mzoughi N, Chouba L (2005) Etude des micropolluants organiques et inorganiques dans les sédiments et les organismes marins du large du Golfe de Gabès. Phys Chem News 22:125–131

Mzoughi N, Chouba L (2011) Distribution and partitioning of aliphatic hydrocarbons and polycyclic aromatic hydrocarbons between water, suspended particulate matter, and sediment in harbours of the West coastal of the Gulf of Tunis (Tunisia). J Environ Monit 13:689–698

Palanques A (1994) Distribution and heavy metal pollution of the suspended particulate matter on the barcelona continental shelf (north-western Mediterranean). Environ Pollut 85:205–215

Romano E, Ausili A, Zharova N, Magno MC, Pavoni B, Gabellini M (2004) Marine sediment contamination of an industrial site at Port of Bagnoli, Gulf of Naples, Southern Italy. Mar Pollut Bull 49:487–495

Saeedi M, Daneshvar Sh, Karbassi AR (2004) Role of riverine sediment and particulate matter in adsorption of heavy metals. Int J Environ Sci Tech 1(2):135–140

Serpaud B, Al-Shukry R, Casteignau G (2004) Adsorption des métaux lourds (Cu, Zn, Cd et Pb) par les sédiments superficiels d'un cours d'eau: rôle du pH, de la température et de la composition du sédiment. Rev Sci de l'eau 7:343–360

Sprovieri M, Feo ML, Prevedello L, Manta D-S, Sammartino S, Tamburrino S, Marsella E (2007) Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). Chemosphere 67:998–1009

Tam NFY, Wong YS (2000) Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environ Pollut 110:195–205

Trefry JH, Nelsen TA, Trocine RP, Eadie BJ (1994) Transport of particulate organic carbon by the Mississippi River and its fate in the Gulf of Mexico. Estuaries 17:839–849

Turner A (2010) Marine pollution from antifouling paint particles. Mar Pollut Bull 60:159–171

Turner A, Millward GE, Le Roux S (2004) Significance of oxides and particulate organic matter in controlling trace metals partitioning in a contaminated estuary. Mar Chem 88:179–192

Uncles RJ, Frickers PE, Easton AE, Griffiths ML, Harris C, Howland RJM, King RS, Morris AW, Plummer DH, Tappin AD (2000) Concentrations of suspended particulate organic carbon in the tidal Yorkshire Ouse River and Humber Estuary. Sci Total Environ 251–252:233–242

Yin J, Falconer RA, Chen Y, Probert SD (2000) Water and sediment movements in harbours. Appl Energy 67:341–352

Zhou JL, Rowland SJ (1997) Evaluation of the interactions between hydrophobic organic pollutants and suspended particles in estuarine waters. Water Res 31:1708–1718

Zvinowanda CM, Okonkwo JO, Shabalala PN, Agyei NM (2009) A novel adsorbent for heavy metal remediation in aqueous environments. Int J Environ Sci Tech 6(3):425–434

Zwolsman JG, Gijsbertus TME (1999) Geochemistry of major elements and trace metals in suspended matter of the Scheldt estuary, southwest Netherlands. Mar Chem 66:91–111